

A KINETIC STUDY OF THE VINYL ACETATE MICROEMULSION HOMO AND COPOLYMERISATION WITH ACRYLIC COMONOMERS IN BATCH AND SEMI-CONTINUOUS REACTORS

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Abstract – The polymerisation of vinyl acetate (VA) in oil-in-water microemulsions stabilized with the anionic surfactant Aerosol OT (AOT) in a semi-continuous reactor to produce a high polymer-content latex was investigated as well as the copolymerisation of VA with (1) butyl acrylate (BuA) in microemulsions (85:15, VA:BuA, w:w) stabilized with sodium dodecylsulfate and AOT (3:1), and with (2) allyl methacrylate (ALMA) in AOT stabilized microemulsions in batch and semi-continuous reactors at 60°C, initiated with potassium persulfate (KPS). The poly(vinyl acetate) nano-latex (23–42% polymer) prepared from the initial microemulsion consisted of 50 nm average diameter particles and average M_n of 1.5×10^5 Da with a bimodal distribution at final conversion (97%). The poly(vinyl acetate-co-butyl acrylate) nanolatex was obtained with 66% conversion, due in part to the electrostatic cage effect (initiator was the positively charged radical - generator, V-50). Copolymer latex particles were 110 nm in average diameter and showed two glass transition temperatures ($T_g = -22.4$ and 44.1°C), indicating the formation of a BuA – rich block initially and a VA-rich block after depletion of the BuA monomer. The poly(vinyl acetate-co-allyl methacrylate) product (reaction initiated with KPS) presented one T_g (41°C). ^1H , ^{13}C NMR spectra indicated that all carbon-carbon double bonds in ALMA reacted forming a slightly cross-linked copolymer.

Introduction

Microemulsion polymerisation is a process for producing colloidal polymers with unique sizes and shapes [1]; it usually requires large amounts of surfactants and yields low polymer-to-surfactant ratios. These drawbacks have hindered the industrial scale-up of microemulsion polymerisation. Microemulsion polymerisation is an alternative process to emulsion polymerisation because it is possible to obtain latexes containing polymeric nanoparticles of high molar mass [1]. However, the kinetics of these two processes is different.

Among the polymers produced by emulsion polymerisation, poly(vinyl acetate) (PVA) stands out inasmuch as more than 20 % of the total production is associated with this polymer [2]. However, because of chain transfer reactions to polymer at high conversions during the emulsion polymerisation of vinyl acetate (VA), highly branched polymers are obtained [3]. On the other hand, in three-component cationic or anionic microemulsion polymerisation of VA, chain transfer reactions to monomer control chain termination, even at high conversions, in contrast to emulsion polymerisation [4].

Sosa et al. [5] reported a method to produce PVA latexes with high-polymer content (ca. 30%) without losing the characteristics of the microemulsion made particles. The method consists of the multi-stage addition of monomer to a latex produced by the polymerisation of 3 wt. % VA in three-component microemulsions stabilized with low concentrations (<1 wt. %) of the anionic surfactant Aerosol OT to produce latexes with up to 30 wt. % polymer.

Microemulsion copolymerisation has been scarcely studied. Candau et al. [6] report a ^{13}C NMR study of the polymerisation of acryl amide (AAM) and sodium acrylate in inverse

microemulsions. They showed that the average copolymer composition is independent of the degree of conversion. Capek and Juranicova [7] copolymerised butyl acrylate (BuA) and acrylonitrile (AN) at 60° C with the water soluble initiator ammonium peroxodisulfate (APS) and dibenzoyl peroxide (DBP) in the organic phase. Capek and Juranicova obtained transparent and stable microlatexes with particle diameters between 40 and 50 nm. Capek [8] prepared stable and bluish microlatexes from the microemulsion copolymerisation of BuA and AN with average particle diameters of 40 nm. In another report, Donescu et al. [9], studied the microemulsion copolymerisation of the system VA: 2-ethylhexyl acrylate (EHA), n-propanol (nPrOH), water, nonyl-phenol etoxilated with 25 moles of ethylene oxide (NPEO₂₅) or the maleic monoester of NPEO₂₅ at 65°C. They report that the probability of microemulsion formation increases as the amount of surfactant or VA in the co-monomer mixture increases and that nanostructure formation is due to the association of nPrOH with water. Pokhriyal et al. [10] studied the copolymerisation of EHA and AN in sodium dodecyl sulfate (SDS) stabilized emulsions and micro emulsions, as a function of initiator concentration, temperature, monomer concentration in the feed and surfactant concentration. The rate of polymerisation was higher in emulsion than in microemulsion. This paper reports recent results of microemulsion homopolymerisation of VA to obtain latex with high polymer content in a semi-continuous reactor and the copolymerisation of VA with butyl acrylate in a batch reactor and with allyl methacrylate in a batch and in a semi-continuous reactor.

Experimental Section

All reactants (purity>98%) except sodium bis(2-ethylhexyl) sulfosuccinate (AOT from Fluka) were purchased from Aldrich. VA and BuA were further purified according to the procedure reported by Perrin and Amarego [11] for ethyl acrylate. All other reactants were used as received. Water was deionised triple distilled grade. 2, 2'-azobis (2-amidinopropane) dyhydrochloride or V-50 (Wako Chem.) was recrystallized from methanol. Argon was ultrahigh purity (99.999%, INFRA).

One – phase micro emulsion regions at 25 and 60° C were determined visually by titrating aqueous solutions of the surfactant (AOT or SDS/AOT 3:1) with the monomer (VA) or mixture of monomers (VA/BuA, 85:15 w/w). Phase boundaries were detected visually at a constant surfactant/water line. Clear samples that did not show static or streaming birefringence when examined through cross polarizers were considered one – phase microemulsions. In the case of ALMA microemulsions, titrations were carried out at 60° C only to determine the maximum concentration of this monomer along H₂O/AOT ratios of 99:1 and 98:2.

For the batch copolymerisations of VA and BuA a 100 mL reactor was used. VA homopolymerisations were carried out along an AOT/H₂O ratio of 1/99 (w/w), 4 wt. % VA and using 1% KPS with respect to the VA as the initiator. The VA/BuA copolymerisations were initiated with 0.1 % of V-50 with respect to the monomer mixture along an SDS:AOT (3:1) to water ratio of 5/95 (w/w) and monomer mixtures of 3.25, 3.75 and 4.25 wt. %. The VA (4 wt. %)/ALMA (1, 2 and 5 wt. % with respect to VA) batch copolymerisations were carried out along an AOT/H₂O ratio of 1/99 and using 1% KPS with respect to the VA as the initiator. Prior to polymerisation, the monomer(s) and the surfactant(s) aqueous solutions were degassed by cooling, pumping and heating cycles. All reactions were carried out at 60° C under argon atmosphere.

The VA homo and semicontinuous copolymerisations were carried out in a 250 mL reactor, started in the batch mode and when the maximum rate of polymerisation ($R_{p_{max}}$) was reached continuous addition of VA or the monomers mixture was initiated by means of a 25 mL gastight syringe (Hamilton 1000 series) and a pump (kd Scientific Series 200 infusion pump). The addition rate of monomer(s) into the polymerisation reactor was at the corresponding $R_{p_{max}}$ ($0.00233 \text{ mol}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$) over a period of 180 min.

Results and Discussion

The partial phase diagram for the SDS/AOT (3:1)/ H_2O / VA/BuA (85:15) system at 25 and 60° C has been reported elsewhere [24] and shows one-phase microemulsions form near the water-rich corner. ALMA microemulsions at 60° C were observed along a H_2O /AOT ratio of 99. The limit of this region contained 0.72 wt. % ALMA.

In the conversion versus time curve for the VA microemulsion polymerisation in a semi-continuous reactor at 60° C it was found that the reaction is fast at the beginning and drops after 4–5 minutes when the semi-continuous addition of VA is started and then monotonically increases again up to final conversion (97-98%, 22.8% polymer) at about 190 min. The latexes appearances evolved from bluish-transparent initially to opaque and white at the end of the process and were stable to coagulation. Sosa et al. [12] report polymer contents close to 30 percent in their stage-wise VA addition process after 480 min of reaction. In both cases the high contents polymer latexes were stabilized with <1 wt. % surfactant (AOT) which is uncommon for any micro emulsion polymerisation process.

The z-average particle diameter (D_z), number average molar mass (M_n) and polydispersity index ($\text{PDI} = M_w/M_n$) at final conversion were 53 nm, 1.5×10^5 Da and 4.0, respectively. The PDI reported by Sosa et al. is 9.6. The molar mass distribution (MMD) found in this study is symmetric and monomodal at low polymer contents but a shoulder evolves at intermediate and high polymer contents indicating the formation of at least a second population.

It was found that the conversion vs. time and rate of polymerisation (R_p) vs. conversion curves for the microemulsion copolymerisation of VA and BuA at 60° C (monomer mixture concentrations: 3.25, 3.75 and 4.25 wt.%) show the typical behaviour observed in microemulsion homopolymerisation: two reaction rate intervals are observed (three intervals in emulsion polymerisation). The rapid increase in the polymerisation rate at the beginning of the reaction is attributed to the high nucleation rate. After reaching the maximum (14–18% conversion), R_p decreases rapidly and then more slowly until final conversion (60-70%). The copolymer formed at the early stages of the reaction is a BuA-rich product until this monomer is used up. Monomer reactivity ratios for VA and BuA microemulsion copolymerisation are $r_{VA} = 0.028$ and $r_{BuA} = 6.219$ [13], thus it is clear that BuA is consumed first. After depletion of the BuA, a VA-rich segment forms until the end of the reaction. The dependency of the maximum rate of polymerisation, $R_{p_{max}}$, on the monomer mixture concentration was determined using a logarithmic plot of the data and the value found was 1.65: $R_{p_{max}} \propto [\text{VA}, \text{BuA}]^{1.65}$. The VA/BuA copolymer shows two glass transition temperatures which agree with the kinetic interpretation given here. The first T_g is close to -23° C which is indicative of a block of BuA-rich copolymer and the second is near 44° C. These values are similar to what is reported elsewhere (Kong et al., -20° C and 36° C). The final average particle diameter was 110 nm.

ALMA is a functional monomer used to create cross linked polymer molecules to improve mechanical and wear-resistant properties to films in coating applications. To achieve this a photo initiator is added into the finished latex so that the cross links form after the coating is applied. Batch reactions were carried out in the system ALMA/VA/H₂O/AOT (1, 2, and 5 wt. % ALMA with respect to VA and semi-continuous polymerisations were performed with 2 wt. % ALMA), both sets of reactions along the AOT/H₂O 1/99 ratio. Conversions in batch reactions were up to 94 % after one hour and in the semi-continuous mode were up to 82 % with a polymer content of 18 % after two hours of reaction. Particle diameters were 30 nm and 50 nm in the batch and in the semi-continuous processes, respectively.

The ¹H NMR spectra of poly(vinyl acetate-*co*-allyl methacrylate) shows the signals associated with PVA that have been reported before [14]. However, the signals corresponding to the allylic protons are not observed. This could be due to the formation of allylic radicals in low concentration that react leading to the disappearance of the allylic group [15]. Thus, the functionality of the allyl methacrylate monomer was lost during the reaction, i. e., both, the allylic carbon-carbon and the vinylic carbon-carbon double bonds, reacted during the polymerisation.

M_n and PDI in the homopolymerisation of VA were 1.3x10⁵ Da and 3.56, respectively, whereas in the copolymerisation of VA and ALMA the values were M_n between 1.1 to 1.2 x10⁵ Da, and PDI between 3.38 to 3.52 in reactions carried out in batch reactors. The incorporation of ALMA does not affect significantly neither the number average molecular weight nor the spread of the distributions as indicated by the PDI. Sosa et al. [12] report similar M_n values for PVA in the micro emulsion polymerisation of VA with a PDI of 5.5. Additional details will be given at the presentation.

Conclusions

The systems SDS/AOT (3:1)/ H₂O / VA/BuA (85:15) at 25 and 60° C and AOT/H₂O/ ALMA at 60° C form o/w one-phase stable microemulsions near the water-rich corner of the diagram. PVA nanolatexes can be prepared with ~23 % polymer content with D_z=53 nm, and M_n = 1.5x10⁵ Da. The MMD of the latex is monomodal initially and evolves into a multimodal MMD at the end of the polymerisation. High polymer contents nanolatexes prepared in a semi-continuous reactor result in a polymer with similar number average molar mass that the one obtained in a reactor operated in a multi-stage addition mode. However, PDI's are substantially different at the same polymer contents.

The kinetics of the microemulsion copolymerisation of VA/BuA (85:15) show the typical behaviour observed in the microemulsion homopolymerisation of these two and other monomers. The maximum rate of polymerisation occurs at 14–18% conversion and shows a 1.65 power dependency on the monomer mixture concentration. The copolymer prepared in this manner is rich in BuA at early stages and becomes richer in VA as the reaction progresses. The copolymer presents two glass transition temperatures: -23° C and 44° C which agree with reported values for this copolymer prepared by emulsion and miniemulsion polymerisation.

A copolymer of VA and ALMA was prepared by microemulsion copolymerisation in both batch and semi-continuous reactors. The acrylic and the allylic carbon-carbon double bonds react due to the long contact times of ALMA in the reactors. Molar masses and PDI's of the poly(vinyl acetate-*co*-allyl methacrylate) copolymer are similar to the PVA homopolymer prepared by microemulsion polymerisation indicating a slight cross linking

reaction between PVA chains due to the incorporation of the functional ALMA monomer into the reaction media.

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